

FLUIDIZED BED UPGRADING OF WOOD PYROLYSIS LIQUIDS AND RELATED COMPOUNDS

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Abstract

The effective hydrogen index (EHI) is a calculated indicator of the "net" hydrogen/carbon ratio of a pure or mixed heteroatom-containing feed, after debiting the feed's hydrogen content for complete conversion of heteroatoms to NH_3 , H_2S , and H_2O . Compounds with EHI's < 1 are difficult to upgrade to premium products over ZSM-5 catalyst due to rapid catalyst aging in continuous fixed bed processing. However, high conversions of such feeds (acetic acid, methyl acetate, and wood pyrolysis liquids) can be maintained in a fluidized bed system operating under methanol-to-gasoline conditions and employing frequent catalyst regeneration. Synergisms observed when coprocessing blends of low and high EHI model compounds also exist for a wood pyrolysis liquid. Thus, when coprocessed with sufficient methanol, the conversion and hydrocarbon yield from wood pyrolysis liquid increased by 19 and 64%, respectively, while coke yield decreased by 40%. A possible processing scheme is described in which the char penalty associated with wood pyrolysis is diminished by gasifying the carbonaceous residue and producing methanol as a cofeed for the synergistic upgrading of the pyrolysis liquids over ZSM-5.

Introduction

Zeolite ZSM-5 is particularly effective for the conversion of methanol to gasoline range hydrocarbons (1). In addition to methanol, other oxygenate feeds, including complex mixtures, can be converted as well (see, for example, references 2-7).

The effective hydrogen index is defined as:

$$(H/C)_{\text{effective}} \text{ or EHI} = \frac{H-2O-3N-2S}{C}$$

where H, C, O, N, and S are atoms per unit weight of sample of hydrogen, carbon, oxygen, nitrogen and sulfur, respectively. Model oxygenate compounds having EHI's <1 produce a poor product slate and cause rapid zeolite catalyst aging in continuous fixed bed MTG processing (3,8) using ZSM-5. Thus, after 2 hours on stream, acetic acid conversion declines from estimated high initial values to <30%. Hydrocarbons account for <10 wt.% of the products from the aged catalyst and, of the hydrocarbon portion, >70% is C₄⁻ (overwhelmingly butenes) and <25% C₅⁺ gasoline.

Cellulosic biomass is a potential source of liquid hydrocarbon fuels. Wood pyrolysis yields carbon-containing liquid products but suffers from two disadvantages. First, a large percentage of the original wood carbon is lost to a low value char by-product. Second, like the model oxygenates described above, the EHI of the liquid products is substantially less than 1.0.

The present study was undertaken to examine the potential of short contact time regenerative fluid bed processing to obviate the problems associated in extended non-regenerative fixed bed operation with such low EHI feeds.

In addition, Chang, Lang, and Silvestri (8) disclosed that reductions in zeolite catalyst aging rate and synergistic yield benefits could be realized in fixed bed operation if the low EHI (<1) feed were co-processed with a sufficient amount of high EHI (>1) constituent. In fixed bed studies, Chantal et al (9) coprocessed up to 10% methanol with an oil derived from supercritical extraction of wood chips. Although some benefits from methanol were evident, the amounts of methanol used were less than those recommended by Chang et al (8), and run durations did not exceed one hour. Consequently, it was not clear if the amount of methanol was sufficient to maximize product yield benefits and to maintain the catalyst's performance in extended continuous processing. It was of interest to us, therefore, to further examine the potential benefits of methanol co-processing for both model compound feeds and wood pyrolysis liquids in short contact time regenerative fluid bed processing.

Experimental

a) Catalyst

The catalyst used was HZSM-5 in a $\text{SiO}_2/\text{Al}_2\text{O}_3$ binder.

b) Production of Wood Pyrolysis Liquids

Sawdust (primarily pine and fir) pyrolysis was carried out at atmospheric pressure and $\sim 520^\circ\text{C}$ in flowing He. The wood charge had the following elemental analysis (dry basis):

C - 49.20%, H - 6.80%, O - 43.40%, ash - 0.60%.

c) Reactor and Run Procedures

All model compound and wood pyrolysis liquid upgrading runs were performed in a computer controlled fluidized bed apparatus (10) (Figure 1) operating cyclically to effect successive and repeated reaction/regeneration intervals. Approximately 35 cc of catalyst was charged to the vycor reactor along with 15 cc of meshed vycor. He fluidizing gas enters through a frit at the base of the tapered section of the reactor bottom. A small flow of He also sweeps through the feed oil sidearm inlet line. The total He flow (850 cc/min.) plus the vapor phase reactant and products maintain the bed in vigorous motion which, in turn, insures good temperature control. Runs were carried out at 1 WHSV based on the low EHI feed component, 410°C and atmospheric pressure. The catalyst was automatically oxidatively regenerated after each 10-20 min. reaction interval.

The product water phase was separated and gc analyzed for oxygenates from which conversion could be calculated. The hydrocarbon product layer contained only a very small amount of oxygen (<1%). Liquid hydrocarbon product was also subjected to gc analysis as were gaseous products, the latter being checked for their hydrocarbon and CO_x contents. Coke was calculated by the computer from on line CO and CO_2 IR data collected during each catalyst regeneration. Elemental and total material balances were generally >95%. Results presented were normalized to a no loss basis.

Results and Discussion

A) Model Compound Conversions

Experimental data are presented in Table 1. Two conversions are presented for each run. "Total conversion" represents the conversion to all products, while "conversion to non-oxygenates" represents conversion to all hydrocarbon, CO_x and H_2O products. The overall yields from the methanol experiment ($\text{EHI} = 2.0$) are in reasonable agreement with data obtained in the fluid bed MTG process (11). The hydrocarbon gas products, however, are higher in propene and lower in isobutane, probably due to the lower reaction pressure used in this study.

A-1) Conversion of Acetic Acid and Methylacetate

The data obtained for acetic acid illustrate several interesting points which can be contrasted with the fixed bed operation cited above. First, total conversions >90% may be maintained indefinitely provided periodic catalyst regeneration is employed. In spite of its having an EHI of 0, which assumes that oxygen is rejected as water, our experimental data show that decarboxylation takes place to a large extent. As a result, by rejecting oxygen as CO_x , substantial production of hydrocarbons is possible. Hydrocarbon liquid product yield is ~80% larger than that obtained at 2 hours processing time in the non-regenerative fixed bed operation (18.3% vs <10%) and ~65% of the hydrocarbon product is C_5^+ gasoline with a predominantly aromatic character. This high selectivity toward aromatics formation is consistent with the low effective hydrogen content of the "hydrocarbon" fraction of acetic acid.

On a weight basis, acetic acid yields only 40% as much hydrocarbon as methanol. The lower yield is primarily due to decarboxylation, and to a small extent, to coke and CO production.

Methyl acetate has an EHI of 0.67 and thus, ordinarily, would also be considered difficult to process. Its net hydrogen content, however, is substantially higher than acetic acid's. Because of its higher carbon content (48.6% C) and despite decarboxylation and coking reactions, the observed hydrocarbon yield remains comparable to that of methanol. Moreover, hydrocarbon selectivity for direct conversion to C_5^+ gasoline is higher than acetic acid or methanol (79.5%). Thus, the direct yield of C_5^+ gasoline is 32.1% on charge vs 23.3% for methanol.

From a hydrogen balance standpoint, both acetic acid and methyl acetate reject less H_2O and more CO_x than methanol, with resultant C_5^+ liquids having effective H/C^+ s of ~1.3 vs ~1.7-2 for methanol processing.

A-2) Conversion of Mixtures of Acetic Acid and Methanol

Processing a 1.9/1 or a 3.8/1 molar mixture of CH_3OH and acetic acid provided observations similar to those already disclosed by Chang, Lang and Silvestri (7), viz, an enhancement in C_5^+ liquid yield at the expense of C_4^- vs what might be expected if the mixture behaved as the average of its two components, the calculated values for which are shown in parentheses in Table 1. The selectivities of the hydrocarbon products amplify the observed synergism with respect to C_5^+ liquids. Furthermore, there is an enhancement in total hydrocarbon yield vs linear combination expectations.

The means by which this is accomplished is illustrated in Figure 2, which shows the effect of increasing mole percent methanol in the MeOH/acetic acid charge and attendant decrease in

oxygen rejection as CO_2 and increase in oxygen removal as H_2O . Thus, more carbon remains available to form hydrocarbon products, much of it becoming C_5^+ liquids.

The above findings demonstrate that short contact time fluid bed reactor operating in a cyclic mode can be used to process low EHI compounds to yield substantial amounts of C_5^+ liquid hydrocarbon products.

By co-processing a low EHI material with a high EHI compound such as methanol, a shift in oxygen rejection from decarboxylation to dehydration takes place. The shift results in an increased yield of hydrocarbons.

The reaction of acetic acid may have potential application in converting fermentation products to hydrocarbons. Acetic acid is a major by-product in bacterial fermentation of biomass to ethanol (12). Mixtures of acetic acid and ethanol may also be processed to hydrocarbons (13).

B) Wood Pyrolysis Liquid Upgrading

The products from sawdust pyrolysis at 520°C in flowing He at atmospheric pressure produced the yields shown in Table 2. Because the object of these experiments was to track the amount of wood carbon which could be converted to hydrocarbons by pyrolysis/ZSM-5 upgrading schemes, the amount of water produced by pyrolysis was not measured, and water in the pyrolysis liquids was fed along with the oxygenate products in subsequent ZSM-5 processing. Elemental analyses and the apparent EHI's (including any water) are presented in Table 3. Inspection of these data indicate that the liquid products contain about 31% of the original wood carbon. The char product accounts for another 49 wt% of the original wood carbon and is available for indirect liquefaction by methanol synthesis. The remaining 20% of the wood carbon becomes CO , CO_2 and methane, about half of which (as CH_4 and CO) is also potentially available for conversion to methanol.

The two pyrolysis liquid layers were homogenized (EHI of the blend was 0.34) by high speed mixing en route to the fluid bed catalytic reactor. The oxygenate conversion obtained at 410°C and 1 LHSV was 67.9% with the product selectivity distribution shown in Table 4A.

Next, the two pyrolysis liquid layers were dissolved in methanol at a 1:1 weight ratio. The solution had an apparent EHI of ~1.3 which meets the recommendations set forth by Chang et al (8). The solution was fed to the reactor at 2 WHSV so that the WHSV based on the pyrolysis liquid feed would be identical to that employed when processing was performed without methanol. In this case, the overall conversion, including methanol, was 90.3 wt%. Under these conditions, methanol alone converts completely and produces ~56 wt% H_2O and 44 wt% hydrocarbon products (11).

Conversion of the pyrolysis liquids (after subtracting the products from methanol) therefore was 80.8 wt%. The selectivity distribution of the net converted products from the pyrolysis liquid is shown in Table 4B.

The results from methanol co-processing are summarized in Table 5. They show diminished decarboxylation, greatly enhanced hydrocarbon yields, greatly reduced coke yields, and improved overall conversion. Thus, with low EHI wood pyrolysis liquids, methanol co-processing has effects similar to those observed for model compounds. In comparison, in fixed bed processing at low methanol concentrations, Chantal (9) also observed conversion enhancements and diminished decarboxylation. Although it was suggested that the presence of methanol may lead to reduced coke yields, the data were variable with increased coke accompanying increased methanol in the feed in several instances. This was likely due to inadequate amounts of methanol co-feed as discussed above. Also, coke yields were fairly high suggesting that the amount of methanol employed would have been insufficient to sustain catalyst performance over extended operating times.

C) Potential Processing Scheme

The advantages of co-processing methanol and pyrolysis liquids are further illustrated by a comparison of two potential process arrangements shown in Figures 3 and 4. A major feature common to both is the use of the pyrolysis char as a cheap source of methanol.

Figure 3 shows the products obtained in a scheme in which direct upgrading of the wood pyrolysis liquids over ZSM-5 occurs in parallel with upgrading of methanol obtained from synthesis gas derived from gasification of the pyrolysis char. In Figure 4, the methanol is mixed with the pyrolysis liquids prior to co-processing over ZSM-5. Approximately 40 lbs. of methanol is potentially available from the char and pyrolysis gas products. This amount would provide a weight ratio of methanol/pyrolysis liquids of 0.73. Since the EHI for this mixture (~1.2) exceeds 1 and is quite similar to that of the 1/1 mixture described above, comparable product distributions should result.

In the parallel processing scheme, a total of 20.6 lbs. of hydrocarbon (~85% C₅⁺ gasoline, including alkylate) per 100 lbs. of total feed (pyrolysis liquid and methanol) is obtained. In the co-processing mode, ~3 lbs. of additional hydrocarbon result concomitant with reduced oxygenates and coke.

Stated differently, without char gasification recycle of pyrolysis liquid oxygenates to extinction over ZSM-5 yields <10% of the original wood carbon as hydrocarbon products. Parallel upgrading of methanol derived from char gasification can increase this value to ~36%, while methanol co-processing boosts the percent of wood carbon transformed into hydrocarbon products to ~42%.

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TABLE 1

410°C, 1 atm., 1.0-1.1 WHSV, 20 min. reaction intervals
HZSM-5 in $\text{SiO}_2/\text{Al}_2\text{O}_3$

	Methanol CH_3OH	Acetic Acid CH_3COOH	Methyl Acetate $\text{CH}_3\text{CO}_2\text{CH}_3$	1.9/1 (molar) MeOH/ Acetic Acid	3.8/1 (molar) MeOH/ Acetic Acid
EHI of Charge	2.0	0.0	0.67	1.0 (1.0)	1.3
Total Conversion	98.6	91.2	89.4	>91 (94.9)	95
Conversion to Non-Oxygenates	98.6	79.8	86.1	90.4 (89.2)	--
<u>Products (Wt.% of Charge)</u>					
CO	0.0	3.7	6.2	2.1 (1.8)	1.1 (1.2)
CO ₂	0.2	31.4	17.6	9.4 (15.8)	5.2 (10.6)
H ₂ O	55.8	28.4	21.5	45.3 (42.1)	48.8 (46.7)
Oxygenates	1.4	20.2	13.9	9.6 (10.8)	5.2 (7.7)
C ₁ Hydro- carbon gas	19.0	3.8	6.0	7.9 (11.4)	9.9 (13.9)
C ₂ Liquid Hydrocarbon	23.3	10.6	32.1	24.9 (17.0)	28.7 (19.1)
Total Hydro- carbons	42.3	14.4	38.1	32.8 (28.4)	38.6 (33.0)
Coke	0.3	1.9	2.7	0.8 (1.1)	1.1 (0.8)
<u>Wt. %'s of Hydrocarbon</u>					
C ₁ + C ₂	5.4	1.5	5.6	7.2	7.6
C ₃ ^o	1.6	0.1	0.7	0.4	0.6
C ₃ ^a	25.9	5.2	6.7	13.8	14.2
iC ₄ ^o	5.5	0.5	0.3	0.4	0.5
nC ₄ ^o	0.4	0.3	0.0	0.1	0.1
C ₄ ^a	5.8	15.7	1.4	1.6	1.9
Total C ₄ ⁻	44.6	23.3	14.7	23.5 (34.0)	24.9 (37.5)
C ₅ ⁺ (gasoline)	54.7	65.0	78.7	74.1 (59.8)	72.3 (58.1)
Coke	0.7	11.7	6.6	2.4 (6.2)	2.8 (4.4)
H/C (effective)* of C ₅	1.7	1.3	1.3	~1.4	~1.4

*Small amounts of oxygen were observed in the C₅⁺ liquid. The use of the effective hydrogen index corrects for this.

Table 2
Wood Pyrolysis at 520°C and 1 atm.

<u>Product</u>	<u>Wt. %</u>
CH ₄	1.4
CO	7.1
CO ₂	8.5
Liquid Oxygenates	55.0
Char	28.0

Table 3
Elemental Analysis, wt%

	<u>Sawdust</u>	<u>Liquid Layer 1 (51%)</u>	<u>Liquid Layer 2 (4%)</u>	<u>Char</u>
C	49.2	25.9	55.0	87.3
H	6.8	8.8	7.5	3.9
O	43.4	65.3	37.5	8.0
Ash	0.6	-	-	No Data
EHI	0.3	0.3	0.6	-

Table 4A
Product Distribution from Conversion
of Wood Pyrolysis Liquids

	wt. %

CO	0.7
CO ₂	10.5
Water	70.7
C ₁ -C ₄	2.5
C ₅ + Hydrocarbons	6.0
Coke	9.6

Table 4B
Product Distribution from Conversion of Pyrolysis
Liquid When Processed in Conjunction with Methanol

	Wt. %

CO	-
CO ₂	-
Water	82.1
C ₁ -C ₄	2.7
C ₅ + Hydrocarbons	11.2
Coke	4.0

Table 5
Advantages Resulting from Methanol Co-Processing

	Pyrolysis Liquids	Pyrolysis Liquids + Methanol (1:1 wt/wt)	% Change
Net Conversion, wt. %	67.9	80.6	+18.7
Hydrocarbons, wt. %	8.5	13.9	+63.5
Coke, wt. %	9.6	4.0	-41.7

FIGURE 1: CYCLIC FIXED FLUID BED APPARATUS

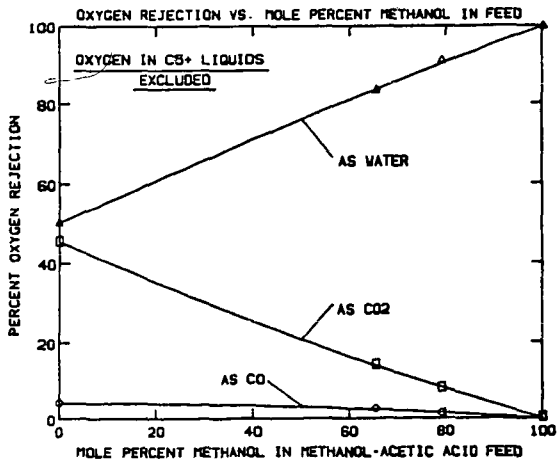
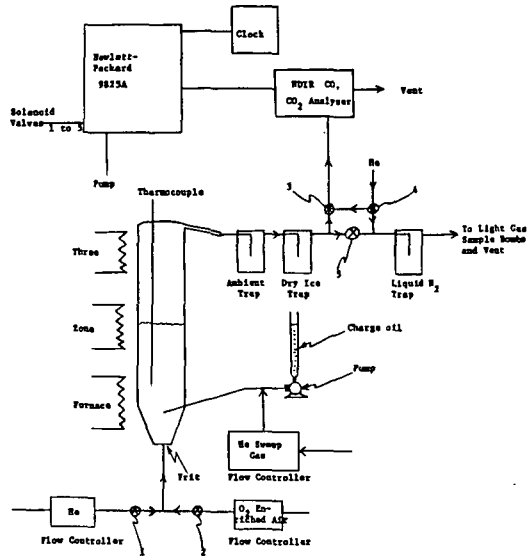


FIGURE 2

FIGURE 3

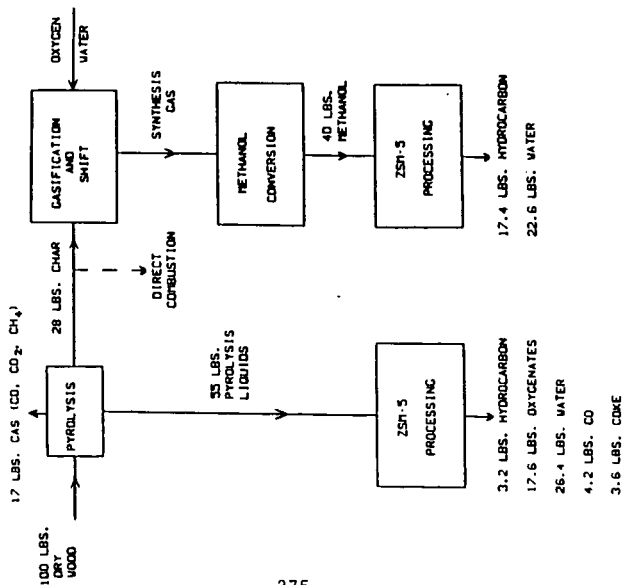


FIGURE 4

